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An Investigation of the Transport Properties of Ion Exchange Membranes

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An Investigation of the Transport Properties of Ion Exchange Membranes

**By J. H. B. George and C. R. Schlaikjer, Arthur D. Little, Inc.,
Cambridge, Massachusetts, for Office of Saline Water; Frank
C. Di Luzio, Director; W. Sherman Gillam, Assistant Director,
Research; H. E. Podall, Chief, Biosciences Division**

**UNITED STATES DEPARTMENT OF THE INTERIOR • Stewart L. Udall, Secretary
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FOREWARD

This is the two hundred and third of a series of reports designed to present accounts of progress in saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea or other saline water.

Except for minor editing, the data herein are as contained in the reports submitted by Arthur D. Little, Inc. under Contract No. 14-01-0001-372, covering research carried out through May, 1966. The data and conclusions given in this report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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I. ABSTRACT

As part of a continuing study of the factors affecting the transport of ions and water through ion exchange membranes, conductivity and water transfer measurements have been carried out in a highly cross-linked organic anion exchange membrane for anions of a variety of charge types. The measurements were made with the membrane in equilibrium with solutions sufficiently dilute so that anion counter-ions were the only conducting species present in the membrane. The measurements were made at several temperatures so that energies of activation might be obtained for the conduction process.

The data for the conductivity and water transfer were combined with estimated values for diffusion coefficients to calculate friction coefficients for the various interactions between the anion counter-ions, membrane, and water. This application of irreversible thermodynamics, while illustrating the interrelationship of the various transport processes, has limited quantitative significance because of certain of the physical assumptions which have to be made in the derivation of the coefficients.

The conductivity measurements have shown that, in contrast with the behavior of cations in a cation exchange membrane, the equivalent conductance of anions in the membrane is not markedly dependent on charge type, at least for moderately sized monovalent and bivalent anions. The conductance does, however, appear to be dependent on interactions with the exchange groups which are more specific or "chemical" in nature. This behavior is probably related to the generally lower degree of hydration of anions as compared to cations.

The data on water transfer show that it is of the same magnitude as that accompanying cation transport in cation exchange membranes. Of considerable interest is the negative coefficient of water transfer observed with ferricyanide. This observation indicates that the original positive charge on the exchange group of the membrane has been converted to a resultant negative charge by interaction with the triply charged anion, giving a membrane with resultant cation exchange properties.

Some measurements have been made of Donnan absorption equilibria in a cation exchange membrane for electrolytes containing cations of a variety of charge types. The finding that the absorption increased markedly with increasing charge on the cation is compatible with the hypothesis of increased ion association indicated by our previous conductivity measurements.

Closer insights into the nature of the interactions between counter-ions and exchange groups are expected from a projected study of "model" systems of solutions of organic acids, bases, and polyelectrolytes of overall composition similar to that of the membrane.

II. INTRODUCTION

The work reported here is a continuation of a general study of the factors affecting the transport of ions and water through ion exchange membranes. Membranes of this type are characterized by a water-insoluble organic polymer matrix having a high water content and containing ionic exchange groups which determine their electrochemical properties. The most common exchange groups are sulfonate ($-\text{SO}_3^-$) for cation exchange membranes and various quaternary ammonium groups ($-\text{NR}_3^+$) for anion exchange membranes. Our previous work with a polystyrene sulfonate cation exchange membrane, as reported in our first annual report,¹ has shown major differences in λ^m , the equivalent conductances in the membrane of counter-ions of various charge types. The ratios of λ^m for monovalent, bivalent, and trivalent cations having very similar equivalent conductances in aqueous solution were found to be approximately 1:3:9. This result appears to be due to ion association, which increases markedly with the charge of the counter-ion.

The major part of the present report is concerned with a study of the behavior of anions of various sizes and charge types through a quaternary ammonium anion exchange membrane whose matrix structure is similar to that of the cation exchange membrane previously studied. Both membranes were prepared by Ionics, Inc., Watertown, Massachusetts.

Systematic data for transport properties of ion exchange membranes over a range of counter-ion sizes and charge types are quite sparse and for anion exchange membranes appear to be nonexistent. Investigations by Manecke and Otto-Laupenmühlen² with phenol-based cation exchange membranes and by Heymann and O'Donnell³ with plugs of cation exchange resins gave results similar to those of this more extensive study. The present work contains measurements, for a wide range of anions, of both equivalent conductance and electro-osmotic water transfer. The measurements were carried out over a series of temperatures in order that activation energies might be calculated for the conduction process.

An ion exchange membrane is a highly interesting physico-chemical system from the standpoint of its transport properties. Its composition makes it resemble a partially nonaqueous solution, and the presence of the exchange groups leads to electrical current being carried only by ions of one sign, at least when the membrane is in equilibrium

with dilute solutions. The polymer structure imposes some size limitations on the passage of ions through the membrane. Of comparable importance is the effect of ion association of the counter-ions with the fixed charges; because of the lower dielectric constant in the membrane, the extent of this association can be expected to be greater than in free aqueous solutions. Conductivity and water transfer measurements are the most convenient techniques for studying these interactions, although they alone cannot distinguish between the two factors which can contribute to the lower values of equivalent conductance--reduced ion mobility and decreased number of charge carriers. Some qualitative indications of the importance of ion association in determining the transport properties of the membrane can be obtained from measurement of the Donnan absorption equilibrium. The Donnan potential in the membrane acts to exclude co-ions (ions having the same sign as the exchange groups), and hence to exclude absorbed electrolyte, and is influenced by the extent of ion association; the absorption of electrolyte is higher the greater the degree of ion association. As part of the present program, some Donnan absorption measurements were carried out on the cation exchange membrane with electrolytes having monovalent, bivalent, and trivalent cations. The results supported the evidence from the previous conductivity measurements.

Future work will include direct measurements of conductivity and ion association, using "model" solutions of organic acids and bases, including polyelectrolyte systems, which correspond closely in overall composition to that of the membrane. Being homogeneous solutions, they should present less experimental difficulty in the determination of ion association constants.

The experimental data on anion transport in the anion exchange membrane have been used in equations derived from the theories of irreversible thermodynamics to calculate friction coefficients for the interactions between the membrane, ions, and water. In this way, it is possible to evaluate the experimental data more systematically than is possible for simple inspection and to bring out the inherent relationship between seemingly unrelated measurements.

The following section describes the details of the experimental procedures used in this work and the experimental results. Section IV contains calculations of the friction coefficients, and a discussion of the significance of the work as a whole is given in Section V.

III. EXPERIMENTAL

The membrane selected for the measurements of anion conductivity and water transfer was a Nepton AR-110 type AZL183 supplied by Ionics, Inc., Watertown, Massachusetts. This membrane has a divinylbenzene cross-linked polystyrene matrix with benzyl trimethylamine exchange groups and was in fact prepared from a polymer matrix having the same formulation (40% nominal divinylbenzene content) as the Nepton CR-61 cation exchange membrane used in the previous work.¹ The membrane is supported on a loosely woven Dynel fabric which contributes about one-third of the weight of the dry membrane. All experiments were carried out with material from the same batch, which was supplied in sheets approximately 9 inches x 10 inches. The membrane was stored in the chloride form and kept immersed in deionized water.

The membrane was converted into various ionic forms by equilibration with solutions of the sodium or potassium salt of the anion concerned, approximately 2N in concentration. The effectiveness of the conversion could be followed by taking samples of the supernatant liquid and testing for chloride by addition of acidified silver nitrate. It was found that, in general, two or three equilibrations were sufficient to convert the membrane completely into the required ionic form. If the anion concerned interfered with the silver nitrate test for chloride, the procedure was modified so that the membrane was first put in the sulphate form. Then the same steps as before were followed, except that acidified barium chloride was used as the test solution. After conversion to the required ionic form, the membrane samples were washed thoroughly with deionized water until no further electrolyte could be leached from them. They then were stored in an excess quantity of a 0.01N solution of the potassium salt of the anion concerned.

Before measurements of conductivity and water transfer were made, the membrane was characterized for capacity, water content, and specific volume by standard methods.

A. CHARACTERIZATION OF THE MEMBRANE

1. Capacity

The capacity of the anion exchange membrane was determined by measurement of the chloride content of a specimen of known weight and dimensions. Specimens of membrane in the leached chloride form were cut into strips, approximately 10 cm x 2 cm, surface-dried with absorbent paper, and weighed. They were then immersed in approximately 50 ml of 2N sodium nitrate solution and equilibrated for 2 hours. The sodium nitrate was then decanted off and replaced with a fresh 50-ml sample. This procedure was repeated until the supernate did not respond to a silver nitrate test for chloride. The combined extracts were then titrated with a standard silver nitrate solution using a potassium chromate indicator. From the titre, the chloride content of the original membrane sample could be calculated. The results of these measurements are given in Table 1.

2. Water Content

The water content of the membrane was determined for all the ionic forms used in these experiments. The procedure involved weighing surface-dried samples of the membrane in the appropriate ionic form and then storing them in a vacuum desiccator at room temperature until constant weight was attained. From the loss in weight, the water content of the membrane could be calculated. Table 2 presents the results of these measurements.

3. Specific Volume

The specific volume of the membrane was determined by measurement of the dimensions of the various specimens whose weight had been determined in the surface-dried condition. A cathetometer was used to determine the length and width of the strips, and the thickness was measured with a micrometer gage. No significant change in volume could be detected when a given strip of membrane was converted into various ionic forms.

TABLE 1

CHARACTERIZATION OF NEPTON AR -110 MEMBRANES*

(Data are for strips 10.0 x 2.0 x 0.058 cm)

<u>Piece No .</u>	<u>Average Thickness (cm)</u>	<u>Weight of Surface-dried Chloride Form (gm)</u>	<u>Capacity (milliequivalents)</u>
1	.058	1.198	0.733
2	.057	1.302	0.763
3	.059	1.268	0.773
4	.059	1.215	0.718
5	.058	1.282	0.773
Arithmetic Mean	.058	1.244	0.752

Thus volume capacity is 0.650 meq/cm^3

weight capacity is 0.605 meq/wet gm

and specific volume is 0.93 ml/wet gm

* These data are for the surface-dried membrane and include the backing material.

TABLE 2

WATER CONTENT OF NEPTON AR-110 IN VARIOUS IONIC FORMS*

<u>Ionic Form of Membrane</u>	<u>Initial Weight of Surface-dried Form (gm)</u>	<u>Final Weight (gm)</u>	<u>Water Content Mean Value (weight percent)</u>
F ⁻	1.3095	0.8770	33.8
	1.4042	0.9199	
Cl ⁻	1.3025	0.9068	29.8
	1.2530	0.8873	
Br ⁻	0.9761	0.6570	32.7
	1.1100	0.7462	
I ⁻	1.3838	0.9549	31.2
	1.2654	0.8682	
NO ₃ ⁻	1.219	0.855	30.4
	1.274	0.880	
ClO ₄ ⁻	1.2582	0.8826	30.4
	1.2070	0.8347	
PF ₆ ⁻	1.3237	0.9348	28.9
	1.1711	0.8378	
CO ₃ ²⁻	1.2182	0.7845	25.4
	1.2123	0.7859	
SO ₄ ²⁻	0.958	0.680	30.2
	1.049	0.720	
Fe(CN) ₆ ³⁻	1.1478	0.8102	29.4
	1.1978	0.8447	

* These data are for the surface-dried membrane and include the backing material.

B. CONDUCTIVITY MEASUREMENTS

The procedure for measuring conductivities of the membrane was essentially that described in the previous annual report.¹ A specially designed conductivity cell holds a disc-shaped sample of membrane parallel to two circular platinized-platinum electrodes so that the current direction is at all times normal to the plane of the membrane. The surfaces of the membrane and the electrodes are separated by a thin film of solution, as shown in Figure 1. An additional refinement on the cell previously used was the insertion of four thin cylindrical bolts through the extremities of the cell to aid in the accuracy of the positioning. Wing nuts were employed to tighten these bolts and a constant torque screw driver ensured that an even pressure resulted.

As in the previous work, the conductivity cell was contained in a small plastic bag and the whole immersed in a constant temperature oil bath. Much care was needed to make certain that complete temperature equilibration was obtained, and particularly to avoid having an appreciable volume of air around the cell. All conductivity measurements were made with the membrane immersed in a 0.01N salt solution, and the membrane resistance was determined by measurements with and without the membrane specimen in the cell. The accuracy of the measurement was greater the higher the resistance of the membrane, but in all cases reproducibility was 3-4% or better. The measuring procedure involved determination of the conductivity at one temperature, for example 25°C, followed by immersion of the plastic bag and its contents in a bath at some other temperature, say 10°C, and determination of the conductivity at the second temperature after thermal equilibrium had been attained. In this way, it was possible to avoid errors due to any change in geometry which might have resulted from taking down the cell. The conductivity determinations were made with a Campbell-Shackleton bridge, capable of measuring resistances to five significant figures. Results of the conductivity measurements and the quantities derived from them are given in Tables 3-6.

C. WATER TRANSFER MEASUREMENTS

The electro-osmotic water transfer accompanying the passage of ions across the anion exchange membrane was carried out in a modified form of the apparatus described in the previous annual report.¹ In the modified apparatus, the membrane separated two chambers of

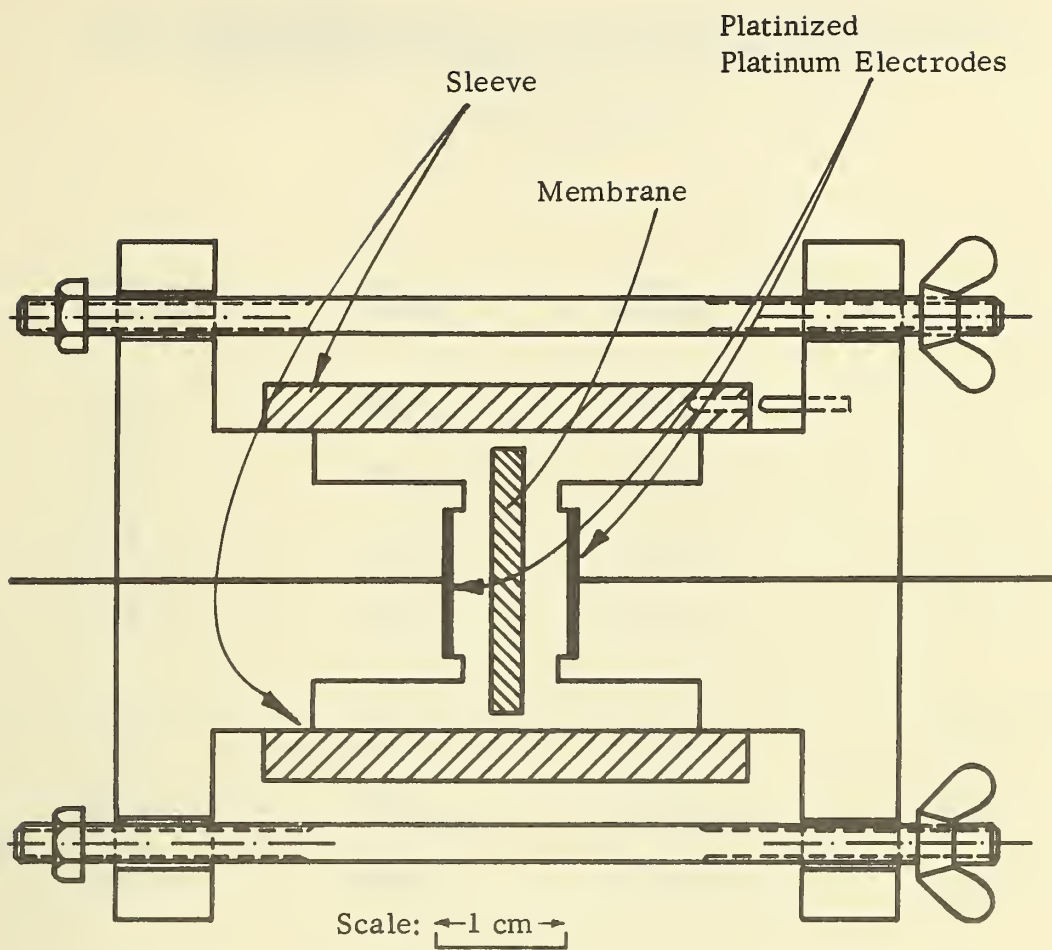


FIGURE 1 CONDUCTIVITY CELL

TABLE 3

SPECIFIC CONDUCTANCES, $k \times 10^3$ FOR NEPTON AR-110 IN
VARIOUS IONIC FORMS AT 10°, 25°, and 40°C
 (ohm⁻¹ cm⁻¹)

	<u>10°C</u>	<u>25°C</u>	<u>40°C</u>
F ⁻	2.86	4.16	5.88
Cl ⁻	2.48	3.65	5.55
Br ⁻	1.52	2.50	3.75
I ⁻	0.70	1.20	1.65
NO ₃ ⁻	1.81	2.78	4.43
ClO ₄ ⁻	0.402	0.652	1.325
PF ₆ ⁻	0.216	0.328	0.503
CO ₃ ²⁻	1.73	3.04	4.69
SO ₄ ²⁻	1.55	2.54	3.69
Fe(CN) ₆ ³⁻	0.0479	0.0736	0.111

TABLE 4

EQUIVALENT CONDUCTANCE λ^m FOR NEPTON AR-110 IN
VARIOUS IONIC FORMS AT 10°, 25°, AND 40°C

(ohm⁻¹ cm² equiv⁻¹)

	<u>10°C</u>	<u>25°C</u>	<u>40°C</u>
F ⁻	4.40	6.40	9.04
Cl ⁻	3.80	5.62	8.23
Br ⁻	2.34	3.84	5.77
I ⁻	1.08	1.85	2.54
NO ₃ ⁻	2.78	4.28	6.80
ClO ₄ ⁻	0.618	1.003	2.02
PF ₆ ⁻	0.332	0.504	0.774
CO ₃ ²⁻	2.66	4.68	7.22
SO ₄ ²⁻	2.38	3.90	5.68
Fe(CN) ₆ ³⁻	0.0737	0.113	0.171

TABLE 5

RATIO $\frac{\lambda^m}{\lambda^0}$, $\frac{\text{EQUIVALENT CONDUCTANCE IN NEPTON AR-110}}{\text{EQUIVALENT CONDUCTANCE IN SOLUTION AT INFINITE DILUTION*}}$

	<u>10°C</u>	<u>25°C</u>	<u>40°C</u>
F ⁻	-	0.115	-
Cl ⁻	0.0700	0.0735	0.0820
Br ⁻	0.0420	0.0493	0.0565
I ⁻	0.0196	0.0241	0.0251
NO ₃ ⁻	0.0553	0.0599	0.0714
ClO ₄ ⁻	0.0129	0.0149	0.0228
PF ₆ ⁻	-	-	-
CO ₃ ²⁻	-	0.0676	-
SO ₄ ²⁻	0.0498	0.0488	0.0516
Fe(CN) ₆ ³⁻	-	0.0011	-

* Values for λ^0 taken from Robinson and Stokes.⁴

TABLE 6

ACTIVATION ENERGIES FOR ANION CONDUCTION
IN NEPTON AR-110

(kilocal/mole)

	<u>Membrane</u>	<u>Solution</u>	<u>Difference</u>
F^-	4.21	-	-
Cl^-	4.56	3.57	+1.0
Br^-	5.30	3.54	+1.8
I^-	5.55	3.28	+2.3
NO_3^-	5.25	3.28	+2.0
ClO_4^-	6.7	3.35	+3.3
PF_6^-	4.9	-	-
CO_3^{2-}	5.9	-	-
SO_4^{2-}	5.1	3.90	+1.2
$Fe(CN)_6^{3-}$	4.9	-	-

dissimilar size. The larger one, the donating compartment, had a capacity of approximately 800 ml and was kept well stirred. The second chamber, the receiving compartment, had a capacity of approximately 100 ml and was connected to a capillary tube which could be used to determine the rate of increase of solution volume in the chamber.

In the experiments with the cation exchange membrane, the apparatus was immersed in a constant temperature oil bath, current passed between silver-silver chloride electrodes, and the change in capillary level measured with the cathetometer. This technique could not be used directly for anion permeable membranes, because chloride ions released into the donating compartment when its electrode acts as a cathode would alter the composition of the donating solution. The result for water transfer would thus be some average of the ion being studied and chloride. To overcome this difficulty a stainless steel cathode was used, and a cathode compartment was built into the donating chamber and separated from it by a cation exchange membrane, as shown in Figure 2. When current was passed through the solution, cations moved from the donating compartment into the cathode compartment where hydrogen was evolved at the stainless steel cathode. During the experiment, fresh solution was from time to time put into the cathode compartment to prevent the accumulation of an excessive concentration of alkali. In this way, contamination of the donating solution was avoided.

When measurements were attempted with the carbonate ion, a problem arose in the receiving compartment of the apparatus. Gas bubbles, presumably carbon dioxide, developed at the anode, and these, of course, vitiated the measurement. To avoid this difficulty, the experiment was carried out with 0.01N sodium chloride solution in the receiving compartment, the membrane being converted to the carbonate form and 0.01N sodium carbonate being present in the donating compartment. The experiment was started immediately after the apparatus was assembled in order to minimize problems due to back diffusion of chloride into the membrane.

The water transfer measurements were carried out at three temperatures, 10°, 25°, and 40°C. The membrane separating the compartments had dimensions of 6 cm x 6 cm and was prevented from buckling by being constrained in a lucite frame. The exposed area of the membrane was about 14 cm², and, with currents of 10 ma being employed in the water transfer measurements, the current density through the membrane was approximately 0.7 ma/cm². At this current density,

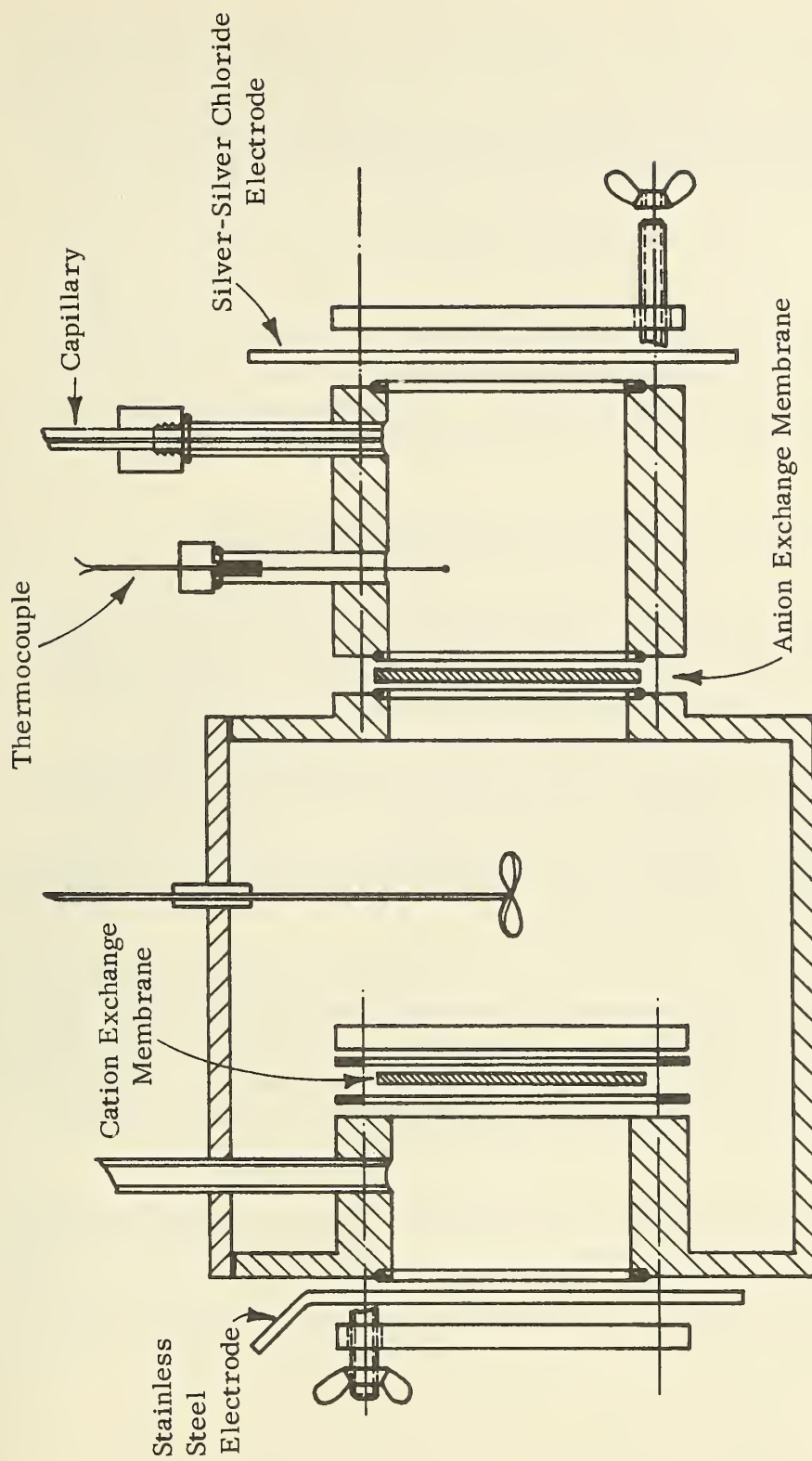


FIGURE 2 WATER TRANSFER APPARATUS

a constant limiting value for the water transfer is attained. Some experiments with cation exchange membranes showed that below about 0.4 ma/cm^2 the observed water transfer increased substantially with the increase in current density. This result may be interpreted as having occurred because only the larger pores of the membrane were used for passage of current (see Figure 6). In our previous study¹ the measurements on water transfer in cation exchange membranes were carried out at a current density of about 0.2 ma/cm^2 and, while self-consistent, are likely to be higher than the average value. The results of the measurements on water transfer accompanying anion transport, however, presented in Table 7, are at a sufficiently high current density to give a true average value for the anion exchange membrane. The scatter in the experimental values indicates that the data have an accuracy of approximately $\pm 10\%$.

D. MEASUREMENTS OF DONNAN ABSORPTION EQUILIBRIA

Donnan equilibrium measurements were carried out at laboratory temperature on the Nepton CR-61 cation exchange membrane. Measurements were made in solutions of sodium chloride, calcium chloride, and lanthanum chloride solutions at concentrations of up to 1.0N. The technique for making these measurements involved equilibration of a membrane sample with the chloride solution of appropriate concentration, followed by surface washing and treatment with a 1N solution of the corresponding nitrate. The nitrate was very effective in flushing out Donnan-absorbed chloride, which could then be determined potentiometrically with a silver-silver chloride electrode.

Particular care was taken in the development of a technique for overcoming the principal experimental problem, that of making certain that no drops of the equilibrating solution were retained by the membrane during the determination of internal co-ion concentration. A satisfactory rinsing technique was evolved by determining the immersion time in distilled water required to wash off surface-held chloride solution.

A membrane sample approximately 3 inches square was allowed to equilibrate in 1N NaNO_3 for several hours. It was then removed, rinsed with distilled water, placed in 1N NaCl for several seconds, removed, and rinsed with distilled water. The membrane was then immersed in chloride-free 1N NaNO_3 , and the solution checked for chloride with the electrodes.

TABLE 7

WATER TRANSFER MEASUREMENTS FOR NEPTON AR-110 IN
VARIOUS IONIC FORMS AT 10°, 25°, AND 40°C(moles faraday⁻¹)

	<u>10°C</u>	<u>25°C</u>	<u>40°C</u>
F ⁻	12.4	11.0	8.8
Cl ⁻	5.7	7.3	6.0
Br ⁻	5.2	7.0	4.8
I ⁻	11.9	11.3	9.7
ClO ₄ ⁻	5.0	6.5	7.9
NO ₃ ⁻	5.3	4.9	5.2
PF ₆ ⁻	8.3	11.4	11.5
CO ₃ ²⁻	5.5	6.3	6.7
SO ₄ ²⁻	3.3	3.0	3.4
Fe(CN) ₆ ³⁻	-9.4	-10.2	-11.9

It was found necessary to soak the rinsed membrane for three minutes in distilled water to remove the sodium chloride trapped in the surface irregularities of the membrane. It is believed that none of this chloride was Donnan-absorbed, since the interior of the membrane would have been occupied by Donnan-absorbed sodium nitrate.

For determination of the extent of Donnan absorption, the 3-inch-square membrane samples were equilibrated overnight at laboratory temperature (23°C) with 1.0, 0.8, 0.6, 0.4, or 0.1N NaCl, CaCl₂, or LaCl₃ in 125 x 65 mm crystallizing dishes. Each membrane in turn was removed from the salt solution, rinsed briefly with distilled water, soaked in distilled water for three minutes, blotted to remove excess water, and immersed in 160 ml of 1N chloride-free NaNO₃, or Ca(NO₃)₂ contained in a crystallizing dish. Donnan-absorbed chloride was displaced by nitrate.

The membrane was swirled in the solution and allowed to equilibrate for 15-20 minutes. The temperature of the solution and the potential of a silver-silver chloride electrode versus a fiber junction reference electrode in the solution were recorded. The data were compared to previously prepared calibration curves, and the concentration of chloride in the solution was deduced. Since the volume of the solution was 160 ml and the aqueous chloride concentration and membrane dimensions were known, the concentration of chloride initially absorbed in the membrane could be calculated.

The results of the Donnan measurements are shown in Figures 3, 4, and 5, in which absorbed chloride (expressed as equivalents of chloride per liter of total membrane volume, including backing) is plotted against external electrolyte concentration. The figures show that Donnan absorption varies linearly with external concentration and that it increases very markedly from sodium chloride through calcium chloride to lanthanum chloride, with slopes in the ratios of approximately 1:2:4. This result appears to give a clear indication of the lower Donnan potential in the bivalent and particularly trivalent forms of the membrane, a finding compatible with an increasing degree of ion association, as shown also by the conductivity measurements presented in our first annual report.¹

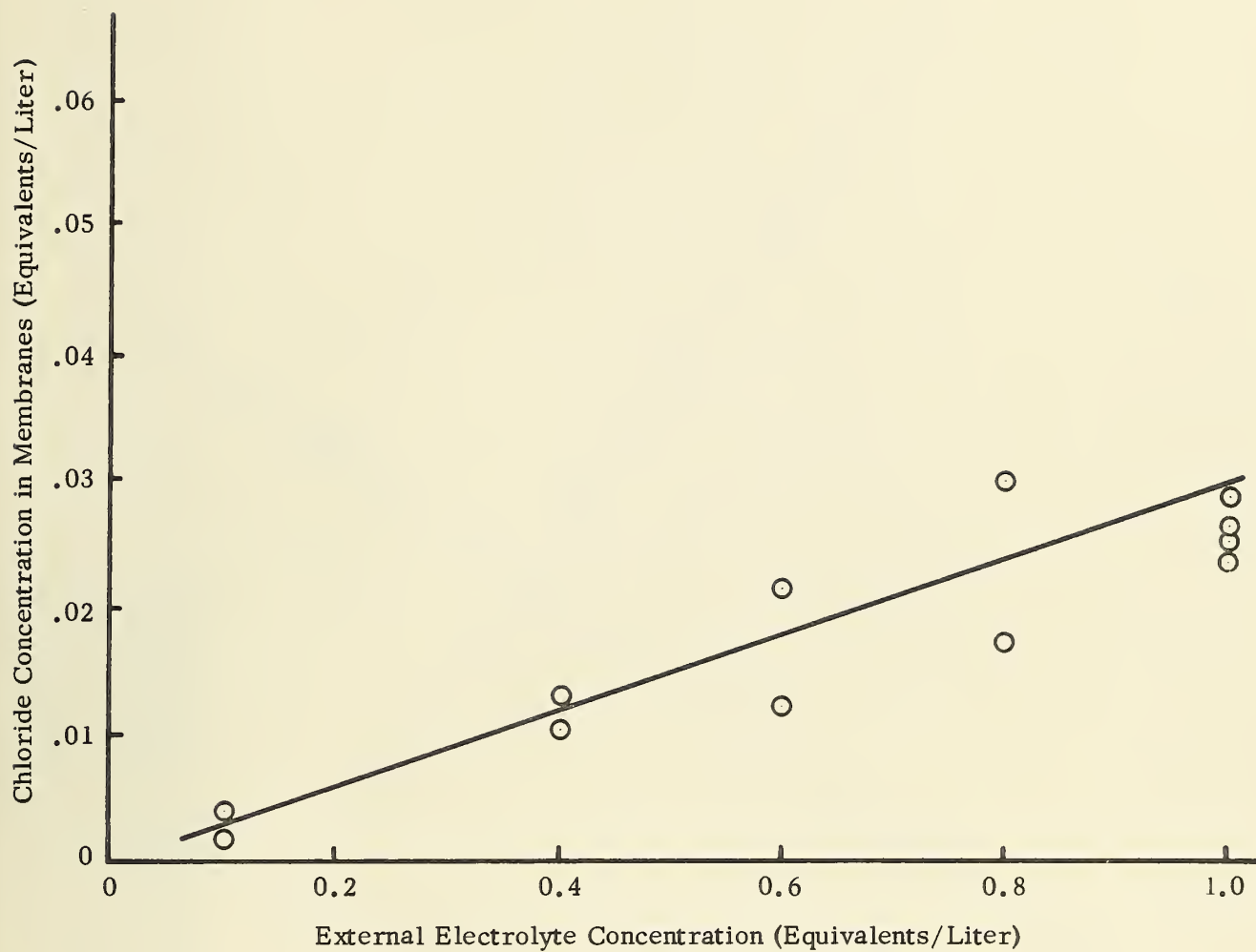


FIGURE 3 DONNAN ABSORPTION OF SODIUM CHLORIDE IN CATION MEMBRANE CR-61

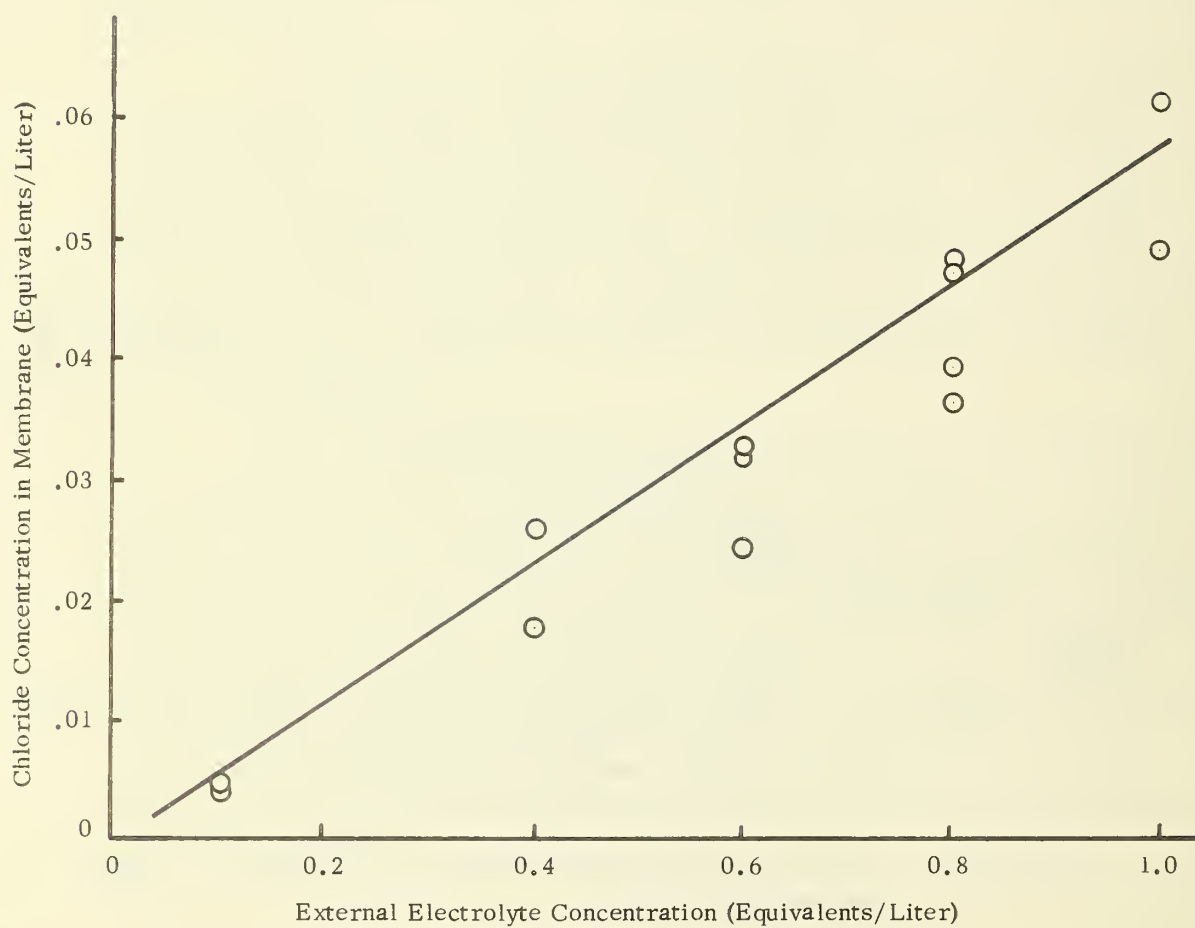


FIGURE 4 DONNAN ABSORPTION OF CALCIUM CHLORIDE IN CATION MEMBRANE CR-61

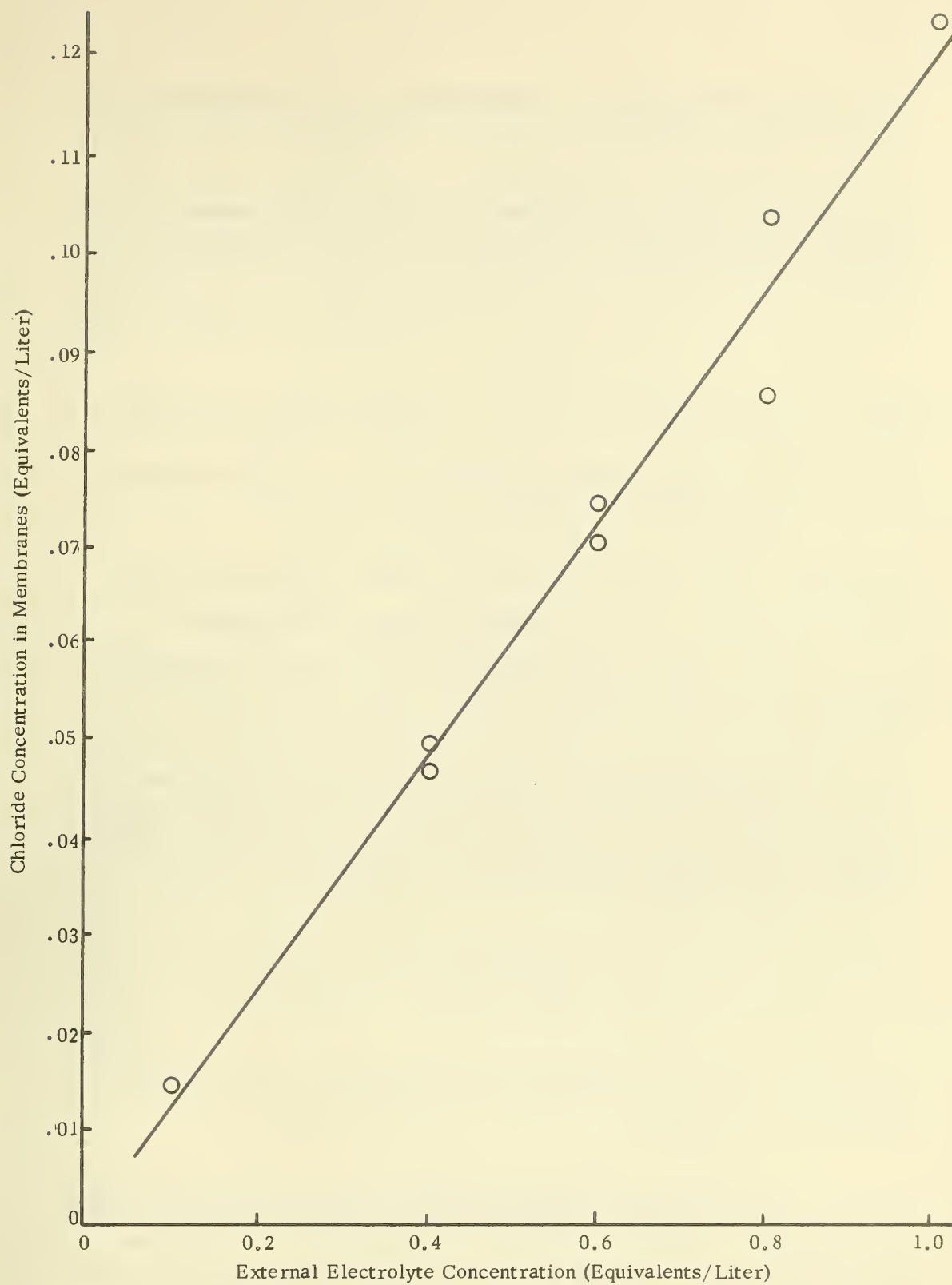


FIGURE 5 DONNAN ABSORPTION IN LANTHANUM CHLORIDE IN CATION MEMBRANE CR-61

IV. THE APPLICATION OF IRREVERSIBLE THERMODYNAMICS

Under isothermal conditions, the steady-state transport of ions and water through an ion exchange membrane can be expressed by equations relating the fluxes to the three generalized forces which can act on the mobile species, viz., electrical, pressure, and diffusional. Thus:

$$J_i = \sum_j L_{ij} F_j$$

where J_i represents the flux of the i th species; F_j represents the total force on the j th species, composed of the terms $-z_j \mathcal{F} \frac{dE}{dx}$ for the electrical force, $-v_j \frac{dp}{dx}$ for the pressure force, and $-\frac{d\mu_j}{dx}$ for the diffusional force; and L_{ij} is a proportionality constant. The symbols $z, \mathcal{F}, E, x, v, p$, and μ have their usual meanings: ionic valency, Faraday's constant, electric field, length coordinate, partial molal volume, pressure, and partial molal free energy, respectively.

In steady-state flow, the total force F_j on the j th species is exactly counterbalanced by the forces of friction with the other species present in the system. According to the simple law of friction, these frictional forces are directly proportional to the relative velocities of the interacting species. Thus:

$$F_j = \sum_{i \neq j} X_{ij} (u_i - u_j),$$

where X_{ij} is the friction coefficient between the species i and j and gives a quantitative measure of the interaction between them, and u_i is the velocity of the i th species.

In carrying out transport experiments in an isothermal system, fluxes J_i can be measured for each species for variations in the three generalized forces: electrical, pressure, and diffusional. The system of interest here, an ion exchange membrane in equilibrium with a very dilute solution, has only three species: the counter-ion, water, and the membrane. Transport phenomena can thus be expressed in terms of three

friction coefficients: X_{13} , X_{14} and X_{34} , representing the interactions between counter-ion and water, counter-ion membrane, and water and membranes, the subscripts 1, 3, 4 referring to the counter-ion, water and membrane, respectively. These quantities can be determined from three experimental measurements and Spiegler⁵ has derived expressions relating the experimentally determinable quantities, ionic diffusion coefficient D_1^m , specific conductivity k , and water transfer W , for a membrane in a given ionic form to the values of the X_{ij} , friction coefficients. Spiegler's expressions are:

$$D_1^m = \frac{RT}{X_{13}}$$

$$k = \frac{z^2 \mathcal{F}^2 c_1 (c_3 X_{34} + c_1 X_{13})}{c_3 X_{13} X_{14} + c_3 X_{14} X_{34} + c_1 X_{13} X_{34}}$$

$$\text{and } W = \frac{c_3 X_{13}}{c_3 X_{34} + c_1 X_{13}}$$

Values for k , W , c_1 and c_3 are available from the experimental data of the previous section. However, no values for D_1^m are available and experimental determination of D_1^m is difficult and time consuming. As was shown in the previous annual report,¹ this quantity can be estimated by (a) correcting values for D_1^0 (the diffusion coefficient for the ion in free aqueous solution at infinite dilution) by an arbitrary factor 0.85, this factor taking into account the increased concentration of ions in the membrane; and (b) dividing by γ_3 , the volume fraction of water in the membrane to compensate for the lower availability of water to the ions in the membrane compared to free solution, and hence for the lower frictional interaction. Thus Spiegler's expression is modified to the form:

$$X_{13} = \frac{\gamma_3 RT}{0.85 D_1^0}$$

and D_1^0 is calculated from the Nernst relationship:

$$D_1^0 = \frac{RT \lambda_1^0}{z \mathcal{F}^2}$$

values for λ_1^0 (the equivalent conductance of the ion in aqueous solution at infinite dilution) being taken from reference 4.

Values for γ_3 and for c_3 , the water content expressed in moles cm^{-3} , can be calculated from the water content of the membrane in the various ionic forms and are shown in Table 8.

Tables 9, 10 and 11 contain values of the friction coefficients X_{13} , X_{34} and X_{14} calculated from the expressions derived by Spiegler.

TABLE 8

 γ_3 AND c_3 FOR NEPTON AR-110 MEMBRANE IN VARIOUS IONIC FORMS

<u>Ionic Form</u>	<u>Water Content wt %</u>	<u>γ_3 Volume Fraction of Water</u>	<u>$c_3 \times 10^3$ Moles cm^{-3}</u>
F^-	33.8	0.364	20.2
Cl^-	29.8	0.321	17.8
Br^-	32.7	0.353	19.6
I^-	31.2	0.335	18.6
NO_3^-	30.4	0.326	18.1
ClO_4^-	30.4	0.326	18.1
PF_6^-	28.9	0.310	17.2
CO_3^{2-}	35.4	0.380	21.1
SO_4^{2-}	30.2	0.324	17.9
$\text{Fe}(\text{CN})_6^{3-}$	29.4	0.315	17.4

TABLE 9

CALCULATED VALUES OF X_{13} ; THE FRICTION COEFFICIENT
BETWEEN COUNTER-ION AND WATER

(Joules sec cm⁻² mole⁻¹ x 10⁸)

	<u>10°</u>	<u>25°</u>	<u>40°</u>
F ⁻	-	0.72	-
Cl ⁻	0.65	0.46	0.35
Br ⁻	0.69	0.50	0.38
I ⁻	0.68	0.48	0.37
NO ₃ ⁻	0.72	0.50	0.38
ClO ₄ ⁻	0.74	0.53	0.40
PF ₆ ⁻			
CO ₃ ²⁻	-	1.20	-
SO ₄ ²⁻	1.33	0.89	0.65
Fe(CN) ₆ ³⁻		1.03	

TABLE 10

CALCULATED VALUES OF X_{34} ; THE FRICTION COEFFICIENT
BETWEEN WATER AND THE NEPTON AR-110 MEMBRANE
(Joules sec cm⁻² mole⁻¹ x 10⁸)

	<u>10°</u>	<u>25°</u>	<u>40°</u>
F ⁻		0.043	
Cl ⁻	0.091	0.046	0.046
Br ⁻	0.110	0.055	0.068
I ⁻	0.027	0.034	0.022
NO ₃ ⁻	0.108	0.080	0.057
ClO ₄ ⁻	0.121	0.062	0.036
PF ₆ ⁻	-	-	-
CO ₃ ²⁻	-	0.059	-
SO ₄ ²⁻	0.152	0.116	0.072
Fe(CN) ₆ ³⁻		0.072	

TABLE 11

CALCULATED VALUES OF X_{14} ; THE FRICTION COEFFICIENT
BETWEEN THE COUNTER-ION AND THE NEPTON AR-110

	<u>MEMBRANE</u> (Joules sec cm ⁻² mole ⁻¹ x 10 ⁸)		
	<u>10°</u>	<u>25°</u>	<u>40°</u>
F ⁻	-	21.5	-
Cl ⁻	30.1	22.0	13.4
Br ⁻	47.3	30.9	18.8
I ⁻	161	74.5	57.7
NO ₃ ⁻	40.7	26.3	16.4
ClO ₄ ⁻	181	119	63.3
PF ₆ ⁻	-	-	-
CO ₃ ²⁻	-	128	-
SO ₄ ²⁻	204	121	86.4
Fe(CN) ₆ ³⁻	-	11,300	-

V. DISCUSSION

The primary objective of this study was to characterize the transport properties of an anion exchange membrane for several anions varying widely in size, chemical nature and charge type. We chose for this study an anion exchange membrane whose polymer matrix structure was similar to that of the cation exchange membrane used in the previous study, thus facilitating comparison of transport behavior in the two types of membrane.

The physical appearance of the anion exchange membrane, Ionics Nepton AR-110 AZL183, was also very similar to the cation exchange membrane Nepton CR-61. Both are structurally reinforced by a loosely woven Dynel backing, amounting to about one-third of the total weight, and must be stored in water to prevent drying out and cracking. The anion membrane is, however, appreciably thinner (mean thickness about 0.058 cm) than the cation membrane (mean thickness about 0.069 cm) and more significantly, it has a very much lower exchange capacity (0.650 versus 1.77 meq per cm³). Water content measurements in various ionic forms range from 25.4% in the carbonate form to 33.8% in the fluoride form (see Table 2). These are lower water contents than were observed in the cation membrane, where values ranged from 32.2% for rubidium to 36.9% for lithium. The membrane water content for various ionic forms appears to follow the generally accepted order for degree of hydration in free solution,⁴ and the average for the cation exchange membrane is higher than for the anion membrane. This provides some evidence that the counter-ions in both types of membrane must retain at least part of their water of hydration.

Several interesting observations can be made concerning the conductivity data presented in Tables 3, 4 and 5. Specific conductivities of the various anions are somewhat lower but of the same general magnitude as those of the cations. The lower capacity of the anion membrane accounts for most of the difference and the membrane equivalent conductances of anions and cations are closely similar. The most distinctive feature of the data derived for the anion membrane is that the equivalent conductances of the bivalent anions, sulphate and carbonate fall in the same range as those of the monovalent anions. This is in very marked contrast to the behavior of the cations, since bivalent cations typically have one-third the conductance of the monovalent cations. The only trivalent anion studied, ferricyanide, had a very low conductance but this may be due as much to its large size as to the triple negative charge.

A comparison of the individual equivalent conductances in the membrane of the halide ions shows a gradual and marked decrease from fluoride to iodide. However, λ^m/λ^0 , the ratio of equivalent conductance in the membrane to that in free solution, for the halide ions decreases much more sharply as is shown in Table 5. The individual values of λ^m for perchlorate and hexafluorophosphate are also very low. These conductance values parallel the general order of ion association constants for these anions with amino nitrogen groups, perchlorate and hexafluorophosphate being especially strongly held. Interaction with the exchange groups thus would seem to be important in determining the conductance of anions in the membrane. The major difference between anion and cation behavior is that in the latter coulombic forces seem to be predominant, since the charge type of the ion is the most important factor, while for the anion specific "chemical type" interaction is more pronounced. This difference can probably be explained by the generally lower degree of hydration of anions which exposes them more closely to the chemical influence of the exchange group.

Activation energies for anion conductance in the membrane, shown in Table 6, are higher than the corresponding values for free aqueous solution and by amounts, which for chloride, bromide and sulphate, at least, are similar to the differences shown by cations. The two values for activation energy differ much more markedly for perchlorate, and, to a lesser extent, for iodide and nitrate. This suggests that a large difference between energies of activation in the membrane and in free solution coupled with a low conductance is an indication of a chemical type of interaction. Low conductance with relatively small differences in activation energies, as in the case of the bivalent cations, may be ascribed to coulombic-type interaction.

Values for the water transfer accompanying the passage of anions across the AR-110 membrane are presented in Table 7, the measurements having been carried out at the same three temperatures, 10°, 25° and 40°, as the conductivity measurements. The current density employed in the water transfer measurements was approximately 0.7 ma/cm². This is sufficiently high to ensure a constant, average value for the membrane. Measurements of the water transfer accompanying the transport of sodium ions across the CR-61 cation exchange membrane as a function of current density showed (see Figure 6) that although a relatively constant value is attained for current densities above about 0.4 ma/cm², the water transfer coefficient rises quite steeply at current densities below this. A similar effect was noted earlier in phenol sulfonic acid membranes

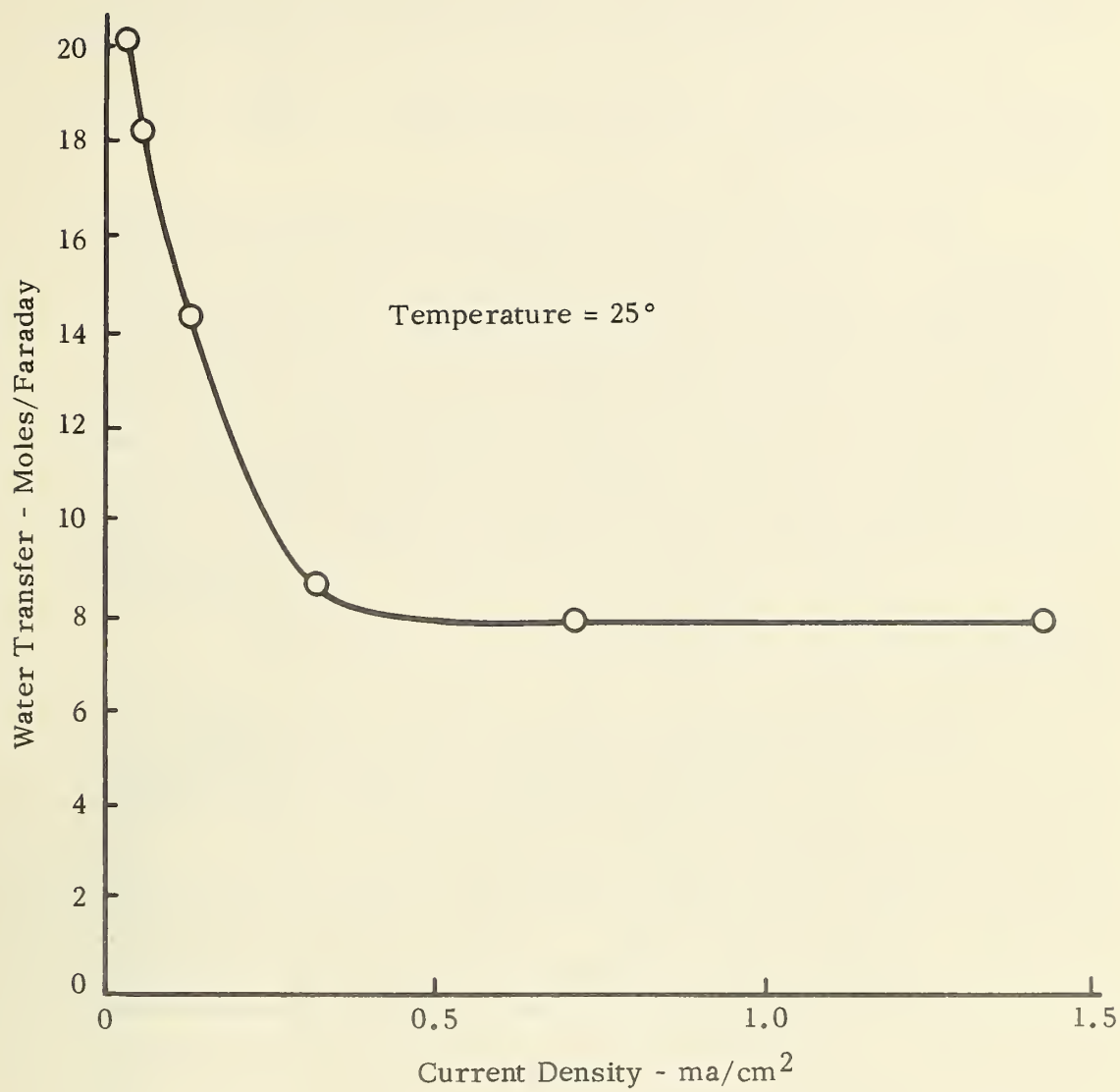


FIGURE 6 WATER TRANSFER IN SODIUM FORM OF NEPTON CR-61 AS A FUNCTION OF CURRENT DENSITY

by Lakshminarayanaiah⁶, who explained the effect with the premise that, at low current densities, only large pores of the membrane are utilized for transport. The measurements on the AR-110 anion exchange membrane are believed to be true average values, but the values reported earlier¹ for cations were obtained at a current density of about 0.2 ma/cm² and, while self-consistent, now appear to be about 50% higher than the constant limiting values. The water transport data for anions and cations cannot therefore be compared directly.

The most interesting data for anion water transfer concerns ferricyanide. The water transfer coefficient is negative, indicating that the water flows in the opposite direction from that of the anions. This strongly implies that interaction between the triple negatively charged anion and the exchange groups has proceeded to such an extent that the exchange groups have acquired a resultant negative charge. The counter-ions are thus positive and the direction of water transfer opposite to what would be expected in an anion exchange membrane. This appears to be the first recorded instance of such interaction leading to what is essentially conversion of an anion exchange membrane into a cation exchange membrane. It is analogous to the previously reported⁷ negative water transfer coefficients for a cation exchange membrane containing tetravalent thorium counter-ions.

Little can be said about the other data for water transfer. The accuracy of the measurements is probably not better than $\pm 10\%$ and it does not seem possible to discern a temperature trend. Water transfer increases with temperature for some and decreases for others but never by very large amounts. Values for the fluoride ion are much larger than for chloride and bromide but the high values for iodide and for hexafluorophosphate are somewhat surprising. The larger anions may possibly block a considerable fraction of the cross sectional area of the membrane pores and exert a mechanical pumping action which may account for the higher values. It is noteworthy that the perchlorate ion, which has an abnormally low equivalent conductance in the membrane, appears to have a normal value for water transfer coefficient.

The experimental results for conductivity and water transfer and the estimated values for diffusion coefficients were used as a basis for calculating friction coefficients for the various interactions in the membrane, following the approach used by Spiegler. Values for the three sets of friction coefficients relating the binary interactions between the counter-ion, water, and membrane are listed in Tables 9, 10 and 11,

respectively. The assumptions made in the calculations of these friction coefficients were discussed in the previous report and they are sufficiently tenuous to limit severely the quantitative significance of the data. Nonetheless the numbers qualitatively are interesting and illustrate the inter-relationships between the experimental quantities.

Numerical values for the friction coefficients are all expressed in the same units of $\text{Joules sec cm}^{-2} \text{ mole}^{-1} \times 10^8$ to facilitate comparison. It can be seen that $X_{14} \gg X_{13} > X_{34}$, i.e., that the interaction between the counter-ion and the membrane (exchange group) X_{14} is greater by about a thousand times than that between the counter-ion and the water X_{13} , which in turn is about ten times greater than that between the water and the exchange group X_{34} . The quantity X_{14} , which is strongly influenced by the value of the membrane specific conductance, k , decreases strongly with temperature but increases with charge on the counter-ion. X_{34} , the interaction between water and the membrane, is small, decreases with temperature and does not vary with charge type, both of which results are as might have been expected. X_{13} , which is calculated for the diffusion coefficients, decreases with temperature and increases with the charge type of the ion.

The usefulness of friction coefficient calculations depends on the validity of the assumptions made in their derivation. The development of independent methods for measuring ion-membrane interactions and extent of hydration would enormously improve the value of this technique for expressing membrane transport properties.

The evidence from the conductivity measurements, expressed also in the high values of the friction coefficient X_{14} , indicates substantial interaction between the counter-ion and the exchange group. The reduced conductivities are, however, probably due partly to a reduced number of charge carriers in the membrane, a result of ion association or "chemical" interaction, and partly to environmental effects such as increased viscosity and physical blocking by the membrane structure. A qualitative indication of the relative contribution of the former effect for different counter-ions can be obtained by determining the extent of Donnan absorption. Some preliminary measurements of Donnan absorption equilibria were carried out on the Nepton CR-61 cation exchange membrane which had been the object of the previous study.

The salts selected for the measurements were sodium, calcium and lanthanum chlorides as representative of mono, bi and trivalent cations.

As seen in Figures 3, 4 and 5, the Donnan absorption appeared to vary linearly over the range of concentrations studied and increases very markedly from sodium chloride through calcium chloride to lanthanum chloride, the slopes having the ratios of approximately 1:2:4. This indicates a decreasing Donnan potential and, without confirming it, consistent with the premise that ion association increases as the charge on the counter-ion increases.

From the measurements presented here and in the earlier report on cation exchange membranes we have developed several insights into the nature of the interactions between exchange groups and counter-ions. It appears that in the case of cation exchange membranes, charge type is the most important determinant of membrane conductivity and that therefore the interaction is largely coulombic in nature. This is not the case in anion exchange membranes where, for example, chloride and sulphate have very similar conductivities. Here the important consideration appears to be "chemical type" interactions with the exchange group, partly a consequence of the lower degree of hydration of anions. Confirmation of these assumptions requires thermodynamic measurements on the membrane system, which, unfortunately, are difficult and time consuming. In the continuing program, it is anticipated that measurements will be made on homogeneous solutions which will act as "model systems" for the membrane. They will be made up of the salts of monomers or polyelectrolytes corresponding closely in composition to that of the membrane and in appropriate concentrations. Measurements on these model systems, in combination with conductivity and water transfer data already obtained, should permit the development of further insights into the nature of the interaction between ions and exchange groups within ion exchange membranes and hence establish a better understanding of membrane transport processes as a whole.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The following tentative conclusions can be drawn from the experimental work to date:

1. The equivalent conductance of cations in sulfonate cation exchange membranes, in equilibrium with very dilute aqueous solutions, is strongly influenced by their charge type. Among cations which have very similar equivalent conductances in free aqueous solution, equivalent conductances in the membrane of monovalent cations are greater than those in the membrane of bivalent cations which in turn are greater than those in the membrane of trivalent cations.

2. This phenomenon does not seem to extend to quaternary ammonium anion exchange membranes where moderately sized monovalent and bivalent anions have similar equivalent conductivities. However, certain anions which are known to interact specifically with quaternary nitrogen groups show low equivalent conductances in the membrane.

3. Thus in cation exchange membranes coulombic type interaction between the counter-ions and exchange groups appears to predominate, while in anion exchange membranes "chemical-type" interaction is more important. The difference in behavior may be due to differences in degree of hydration. The more heavily hydrated cations behave as "charged spheres" with water molecules on their periphery. The behavior of the less hydrated anions appears to be determined more by their chemical nature.

4. Measurements of Donnan absorption equilibria on the cation exchange membrane are consistent with the hypothesis that ion association increases with increasing charge on the counter-ion.

5. Water transfer accompanying the transport of both anions and cations through the membrane is of the same general magnitude, although values tend to be higher for cations, such as lithium, which are known to be heavily hydrated. No definite trend was observed in the magnitude of water transfer as a function of temperature.

6. Water transfer measurements on the anion exchange membrane containing the triply negatively charged ferricyanide ions show that the flow of water is in the opposite direction to that of anion transport. This indicates that interaction with the counter-ion has essentially converted the membrane from being an anion exchanger to a cation exchanger.

7. Application of the equations of irreversible thermodynamics to the transport data effectively demonstrates the interrelationship between the experimentally determined parameters. It has little detailed significance, however, because of the physical assumptions made in the derivation.

B. RECOMMENDATIONS

To increase our understanding of membrane transport phenomena more experimental work is clearly desirable to:

1. extend the measurements of conductivity and activation energy of conduction to a wider range of cations and particularly anions; and to
2. attempt to determine the relative contribution of (a) interaction of counter-ions with exchange groups which reduces the effective number of charge carriers; and (b) environmental factors, which affect their mobility, on the observed membrane conductances.

Kinetic and thermodynamic measurements on the same system are required to determine the roles of interaction and environment and, since thermodynamic measurements are experimentally difficult in membrane systems, it appears more profitable to carry out a more extensive series of measurements in "model systems" composed of salts of organic acids and bases, including polyelectrolytes, chosen to approximate the overall composition of the membrane. Implementation of such measurements will be a primary task of the continuing program.

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